

TRANSPORT OF WATER IN CATION EXCHANGE MEMBRANES
II. INFLUENCE OF POLARIZATION LAYERS
IN NATURAL CONVECTION

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| 16. Abstract The interfacial concentrations of an ion-exchange membrane polarized by electrodialysis in vertical natural convection have been measured by a method using the concentration overpotential between the two sides of the membrane. If suitable experimental conditions are chosen, profiles for which the interfacial concentrations are identical on both sides can be obtained. Under these specific conditions measurement of the water flux gives the so-called pure electroosmosis; therefore the water-transport number is independent of the current density. However, in the general case of a polarized membrane, below the limiting current density, the water transport number is found to be current-dependent. A theoretical analysis of the system using both membrane parameters and hydrodynamics in the diffusion layer has been developed; it provides an interpretation of the observed phenomena as well as of previous results described in the literature. | | | |
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NOTATION LIST

| | |
|------------------------------|--|
| a : | Numerical coefficient of Equation (1). |
| l : | Membrane thickness |
| g : | Acceleration of gravity. |
| h : | Average height of membrane. |
| t_1 : | Transport coefficient of the counter-ion in the membrane. |
| t_1^0 : | Transport coefficient of the same ion in solution. |
| $t_{o(app)}$: | Apparent water transport coefficient |
| t_{GE} : | Transport coefficient of water obtained by the EQUI method. |
| t_{OD} : | Transport coefficient of water obtained by the DICET method. |
| t_{OE}^* : | Coefficient defined by Equation (16). |
| A, B, G : | Coefficients defined by Equation (8). |
| c, c_m, c_{ap}, c_m, c_m : | Concentrations of solutions of NaCl defined in Figure 1. |
| ΔC : | Concentration difference in diffusion films (Figure 1). |
| D_S : | Diffusion coefficient of salt in solution. |
| F : | Faraday |
| I : | Current density. |
| I_E, I_D : | Current densities corresponding to methods EQUI and DICET, respectively. |
| J_i : | Molar flux density of species i . |
| J_S : | Molar flux density of salt in the membrane. |
| J_{diff} : | Diffusion flux density in the films. |
| J_V : | Volume flux. |
| K_D : | Proportionality coefficient between ΔC and $I^{4/5}$ obtained by the DICET method. |
| K_E : | Coefficient introduced in Equation (2). |

L_{ik} : Coupling coefficients.
 M_i : Molar mass of species i .
 P : Hydrostatic pressure.
 P_1, P_2 : Permeability coefficients measured with and without current, respectively.
 R : Perfect gas constant.
 R_{ik} : Friction coefficient
 T : Absolute temperature.
 \bar{V}_i : Partial molar volume of species i .
 ω, ξ, ϕ : Coefficients defined by Equations (12) (13).
 δ : Nerst layer thickness.
 ϵ : Density coefficient of a saline solution.
 φ : Electrical potential.
 η_i : Electrochemical potential of species i .
 μ_i : Chemical potential of species i .
 ν : Kinematic viscosity
 Φ : Osmotic coefficient.
 θ : Entropy production in the membrane.
 $0, 1, 2$: Subscripts corresponding to water, the counter-ion and to the co-ion.

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INTRODUCTION

An ion exchange membrane subjected to a concentration gradient or an electrical field perpendicular to its surface surrounds itself with polarization layers produced by the discontinuity of ionic mobilities at the membrane/solution interfaces.

Three approaches can be used for studying the trans-membrane transports in this case.

- Consider the film/membrane/film sandwich on a global scale: the parameters obtained then are obvious. This is the method used by a number of authors.

- Research the influence of the polarization layers on the measured values in order to obtain more specific parameters for the membrane medium. This was in particular done in the electrolyte diffusion studies [1, 2, 25, 26]. On the other hand, /830

* Numbers in margin indicate pagination in original foreign text.

for water transport measurements, Bary and Hope [3] made corrections for the case of a natural vegetable membrane. Recently Kobatake [31] did this with the membrane PS 1.

- Modify the characteristics of the diffusion films in such a way that the experimental measurement does not involve the polarization. In general, a great deal of agitation is produced in order to reduce as much as possible the diffusion layer thicknesses [4]. Here we have attempted to break away from the polarization layers, not by eliminating them but by imposing special profiles on them.

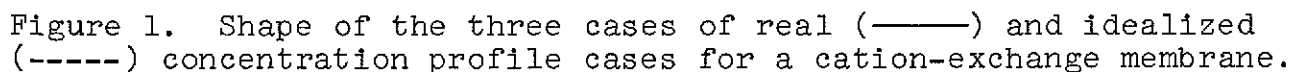
For water transport we will present a comparison between the results obtained for various types of imposed concentration profiles.

I. Problem Formulation

In the case of an isobaric and isothermal system, the various osmotic and electroosmotic water fluxes are controlled by the following parameters:

- the current density which controls the electroosmosis;
- the interface concentrations which control the osmosis;
- the characteristics of the membrane on which the electrochemical potentials and the mobility of the various species depend.

The interface concentrations are a characteristic of the modifications introduced by the polarization. Therefore, they take into account the three modes of transport inside the diffusion films to the region outside of the membrane: electromigration, diffusion, convection.

 Δc : concentration difference in the diffusion films.

By selecting the particular concentration profiles in the case where the interface concentrations are known, it is possible to isolate the relative contributions of osmosis and electro-osmosis in the measured water transport.

We will assume that the profiles shown in Figure 1 can be obtained in reality. A discussion about the restrictions to be made for realizing them in experiments will be presented later on.

1) Profile (a)

An exchange membrane for cations separates two NaCl solutions with the concentrations $C^{\circ}_{(I)}$ and $C^{\circ}_{(II)}$, which are selected so that their arithmetic mean is C (reference concentration is 10^{-1} M here). No electrical current will pass through the membrane and, if a sufficiently effective convection is maintained at the interfaces, the concentration polarization can be ignored.

The measurement of water transport under these conditions leads to a measurement of the osmotic flux.

2) Profile (b)

The membrane separates two solutions with the preceding concentrations $C^o_{(I)}$ and $C^o_{(II)}$.

A current density I is applied such that the polarization produced will lead, for the established regime, to the same interface concentrations to each side of the membrane.

This profile is of interest because there is no concentration gradient in the membrane, and the osmotic forces are in equilibrium.

Under these cases, it is possible to obtain purely electro-osmotic flux.

3) Profile (c)

This profile can be considered as a combination of the two preceding ones as a first approximation.

In effect, the interface concentrations $C_{(I)}$ and $C_{(II)}$ are the same as for the profile (a) and the concentration difference in the films (ΔC) is the same as in profile (b) (which does not necessarily mean that the current density is the same).

In this case, the measured water transport is a combination of the osmotic and electroosmotic fluxes.

Therefore, a meaningful discussion can be carried out about the change in the apparent water transport coefficient brought

about by the polarization. In the following we will discuss how these concentration profiles can be imposed as well as how the water transport was measured, before we discuss the results found.

II. Measurement and Control of Interface Concentrations

The various desired polarization profiles shown in Figure 1 are a consequence of the type of convection which develops at the membrane interfaces.

The profile case (a) is easily resolved: a simple agitation by small magnetic bars is enough to make the films which are the result of the electrolyte diffusion in the membrane negligible.

For the two other profiles, if there is an electrical field, it is known that no matter what type of convection is imposed on a vertical wall, the thicknesses of the diffusion layers (or the concentration gradients at the interfaces) are not constant at every point of the interface [5].

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An additional study on natural convection [6] showed that under the proposed experimental conditions, the utilization and determination of average variables (thicknesses of the Nernst layers and interface concentrations) can be used to describe the polarization with an accuracy which is sufficient and which distinguishes the various independent methods in a correct manner.

On the other hand, it is important for the production of the profiles (b) and (c) to obtain identical diffusion layer thicknesses on each side of the membrane. We have also shown [6] that natural convection brings about average thicknesses of the diffusion layer which are practically equal.

Even though they are locally the same (at the top and at the bottom of the membrane), the concentration profiles are not exactly those desired. Because of compensation phenomena, we can hope that the membrane will react as though all of the points would be subjected to the same concentration profile. This hypothesis is apparently a limitation of the method and we will discuss it in Part IV.

The measurement and creation of profiles (b) and (c) were previously described [7] and were known by the names EQUI method (Equal concentrations imposed at the Interfaces) and DICET method (Determination of Interfacial Concentration by Extrapolation as a function of Time).

We will rapidly summarize the principle of these methods. The measurements are based on the determination of the concentration overvoltage potential at zero time when the electro-dialysis current is interrupted [8].

This potential is produced by studying the relaxation diffusion of the concentration profiles, for which the law obeys a function of the square root of time [7].

If the electrochemical properties of the membrane and the solutions are known beforehand, it is possible to calculate the concentration profiles.

In the case of profile (c), the concentrations are equal before the current passes and a polarization Δc corresponds to each current density. By measuring the overvoltage potential, we can directly relate I and Δc .

In the case of profile (b), the concentrations of the solutions are selected such that equal concentration is produced along C. The corresponding current density (I_E), however, cannot be found a priori. In an experiment one can plot the overvoltage potential as a function of the current density. The calculation of the theoretical overvoltage potential for equal concentration leads to the current density of equal concentration by means of an interpolation.

This must be repeated for each concentration pair $C^o_{(II)}$ and $C^o_{(I)}$ such that I_E can be plotted as a function of the imposed Δc . It does become possible to make the electromigration flux vary for the constant characteristics at the membrane interfaces.

These two methods make it possible to experimentally relate I and Δc using different methods.

Let us already note that any difference obtained between the results for each of the two profiles will be the indication of a very permeable membrane, for which the osmosis and retro-diffusion cannot be ignored. Therefore it is possible to express this difference by calculating the flux resultant and by utilizing the natural convection loss.

The general law of natural vertical mass convection transfer at the level of a polarizable interface is given by the nondimensional formula [9] (here we are referring to average values of Nu and Gr)

$$Nu = a(Gr \cdot Sc)^{1/4} \quad (1)$$

$$\begin{aligned} \text{where } Nu: \text{ Nusselt number} &= \frac{J_{diff} h}{\Delta C D}; \\ Gr: \text{ Grashof number} &= \frac{h^3 g \alpha D}{\nu^2}; \\ Sc: \text{ Schmidt number} &= \frac{\nu}{D}. \end{aligned}$$

(See the definition of the symbols in the appendix);
 a = numerical coefficient determined experimentally (for our system $a = 0.595$) [6].

The expression for the Nusselt number varies according to whether one is studying profile (b) or (c).

1. Profile (b).

If we ignore the modifications in the solution concentrations caused by electroosmosis, it is easily shown from the flux balance at the interfaces of the membrane that

$$Nu = \frac{h(t_1 - t_1^0)I}{\Delta C D F}$$

and when substituted in (1) we find

$$I_E = K_E (\Delta c)^{5/4} \quad (2)$$

with

$$K_E = \frac{a F D}{t_1 - t_1^0} \left(\frac{v}{D} \right)^{\frac{1}{4}} \left(\frac{g \alpha}{v^2} \right)^{\frac{1}{4}} h^{-\frac{1}{4}}$$

2. Profile (c).

In this case, the interface concentrations are not equal and osmotic and retrodiffusion fluxes appear in the balance equation.

As Hellferich [10] has shown, we will use a global permeability coefficient (P_1) with a limited theoretical validity. However, it can be utilized by using the external concentrations as a reference:

$$J_s = P_1 \frac{2 \Delta C}{l}$$

If as before we ignore the concentration modifications caused by electroosmosis, the expression for the Nusselt number becomes:

$$Nu = \frac{h_1(t_1 - t_1^0)l}{\Delta C D F} - \frac{2 P_1 h}{I_D}$$

and if we substitute Equation (1), we find

$$I_D = K_E (\Delta c)^{5/4} + \frac{2 P_1 F \Delta c}{l(t_1 - t_1^0)} \quad (3)$$

If in the experiment one finds a significant difference between the intensities required for the two profile cases for obtaining the same polarization Δc , the term P_1 can be calculated:

$$P_1 = \frac{(I_D - I_E)l(t_1 - t_1^0)}{2 F \Delta C} \quad (4)$$

The plot of the curves $I = f(\Delta c)$ depending on the two methods represents a new approach to the problem of the permeability of an ion exchange membrane. On the other hand, the optimum experimental conditions are thereby known in order to perform true water transport measurements. /822

III. Water Transport

In accordance with Katchalsky and Curran [20], we can express the entropy production inside the membrane for an isothermal system by means of the relationship

$$\theta = \sum_{i=0}^{i=2} J_i \Delta \eta_i \quad (5)$$

$i = 0, 1$ and 2 for the water, the cation and the anion, respectively.

$\Delta \eta_i$ is the difference in electrochemical potential between the two external faces of the membrane (continuity of the electrochemical potential at the membrane/solution interface).

$$\eta_i = \mu_i + z_i F \varphi + \bar{V}_i P$$

In a region not too far from equilibrium (5) can be written as follows in a linear form

$$\Delta \eta_k = \sum_{i=0}^2 R_{ki} J_i \quad (6)$$

$$J_i = \sum_{k=0}^2 L_{ik} \Delta \eta_k \quad (7)$$

The coefficients L_{ik} and R_{ik} must satisfy the Onsager reciprocity relationship [21].

If we write (7) for the water flux and if we replace $\Delta \eta_1$ and $\Delta \eta_2$ by their expressions as a function of the flux (6), we obtain the following after rearranging [11]:

$$J_0 = -A \Delta \mu_0 + B J_1 + G J_2 \quad (8)$$

A, B, G are linear combinations of L_{ik} and R_{ik} which only depend on the concentrations and the temperature. In addition, we can express the difference in the chemical potential of the water as a function of the various interface concentration differences, assuming that the osmotic coefficient varies only slightly within the concentration range studied [22].

$$\Delta \mu_0 = -\frac{2 R M T M_0 \Phi}{1000} (C_{(m)} - C_{(n)}) \quad (9)$$

a) Osmosis, profile (a)

In the case of profile (a), the chemical potential difference of the water between the two compartments produces an osmotic flux directed towards the concentrated solution. For uncharged membranes, the flux is proportional to the osmotic pressure difference. On the other hand, for the ion exchange membranes, one often

observes anomalies [11, 12, 13]. The flux is either higher (abnormal positive osmosis) or smaller (abnormal negative osmosis) than the theoretical flux.

Various theories have been developed for taking into account these phenomena [14, 15, 16, 17].

We will follow the development of Tasaka [11]. This author starts with Equation (8) and expresses the salt flux by Equation (10). We should note that in the case of osmosis we have

$$J_1 = J_2 = J_3.$$

$$J_s = P_2 \frac{(C_{(u)}^o - C_{(u)}^o)}{l} \quad (10)$$

Let us note that the permeability coefficient P_2 depends strongly on the concentrations used [11].

The volume flux is defined by the equation

$$J_v = J_0 \bar{V}_0 + J_1 \bar{V}_1 + J_2 \bar{V}_2 \quad (11)$$

By combining Equations (8), (9), (10), (11), one finds the following expression for the osmotic flux:

$$J_v = \omega(C_{(u)}^o - C_{(u)}^o) + \xi P_2(C_{(u)}^o - C_{(u)}^o) \quad (12)$$

where

$$\omega = \frac{2AV_0RTM_0\Phi}{10^3}$$

$$\xi = \frac{\bar{V}_0(B+G)}{l} + \frac{\bar{V}_s}{l}$$

In Equation (12), the first term of the right hand part represents the purely osmotic contribution, whereas the second term is the contribution caused by electroosmosis.

b) Electroosmosis, profile (b)

When profile (b) has been realized, there is no concentration gradient in the interior of the membrane, which is assumed to be isotropic. This makes the osmotic flux zero as well as the retrodiffusion of the salt. On the other hand, the applied electrical field produces an electroosmotic flux. This flux is brought about by the fact that it is impossible for the charges carried by the membrane to migrate in the electrical field.

The motion of the water takes place in a sense that there is migration of compensating ions. Therefore, this provides a relative motion of charges which are fixed with respect to the barycenter of the system.

The measurements of electroosmotic flux carried out by numerous authors seem to come close to each other in this case.

In effect, the influence of polarization films is minimized by the agitation of solutions which contain a membrane. Nevertheless, it should be noted that it is impossible to completely suppress them and that the measurements are always afflicted with this systematic error.

We will characterize the membrane by its apparent water transport coefficient defined by the following equation:

$$t_{0(\text{app})} = \frac{J_v F}{V_0 I} \quad \Bigg|$$

(this definition differs slightly from the one generally used because here the contribution of the salt is included in J_v).

According to Equations (8), (11) and (2) it is possible to express the water flux as a function of the current density or of ΔC .

$$\begin{aligned} J_v &= \psi I = \psi K_E \Delta C^{3/4} \\ F\psi &= \{t_1[(B + G)\bar{V}_0 + \bar{V}_s] - G\bar{V}_0 - \bar{V}_s\} \end{aligned} \quad (13) \quad \underline{/823}$$

and the water transport coefficient

$$t_{0E} = \frac{\psi F}{\bar{V}_0} \quad (14)$$

We have set $\Delta\mu_0 = 0$ because there is no concentration gradient between the membrane faces. Equation (13) shows that the water flux must be proportional to the current density which is used, which is in general observed or even better. One finds that the water coefficient is constant no matter what I is (less than the critical current density). The parameters B and G only depend on the concentrations which remain constant under various experimental conditions.

Most of the results given in the literature show that the water transfer coefficient and the current density are independent. However, in a few cases [18, 19, 4], t_{0E} increases very strongly at low current densities and goes to a limit at higher currents. Various mechanisms have been proposed to explain this phenomenon. More detailed developments can be found in the work of Lakshminarayanaiah [4].

c) Electroosmosis, profile (c)

It does not seem that the measurements of water flux have been made with such a system. In effect, in this case, the flux measured with the effect of an electrical field is complex. There results a combination of an electroosmotic flux and an osmotic flux, which is created by the concentration difference at the interfaces.

The combination of Equations (8), (9) and (11) makes it possible to express J_V as follows for the general case:

$$J_V = \omega(C_{(II)} - C_{(I)}) + \psi I \quad (15)$$

and the water transport coefficient is

$$t_{0D} = t_{OE}^* + \frac{2\omega F \Delta C}{V_0 I} \quad (16)$$

Equation (16) indicates that the water transport coefficient is a result of the addition of two contributions, one a purely electroosmotic contribution (t_{OE}^*) and an osmotic contribution.

In the general case, one would expect that the water transport coefficient depends on the current density.

Let us note that t_{OE}^* is written in a form which is analogous to t_{OE} and is equal to it when $\Delta C \rightarrow 0$ and $I \rightarrow 0$. On the other hand, in the case (b), one must not assume that ψ is constant when I varies, because the gradients in the membrane are changed as a function of the polarization.

IV. Experimental Results

We will present results concerning two homogeneous cation exchange membranes which are not of commercial origin and which have the general properties given in Table I.

These two membranes were selected because of the important difference which exists between their water content, whereas their transport coefficients are essentially identical.

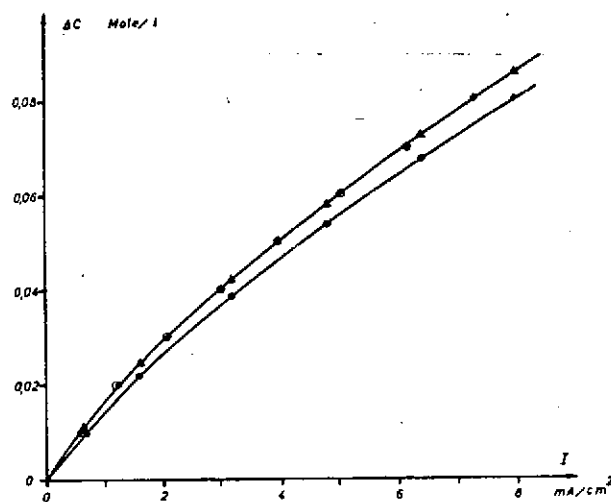


Figure 2. Variation of the concentration differences in diffusion layers as a function of current density.

- Membrane B, method DICET.
- Membrane B, method EQUI.
- ▲ Membrane A, method DICET.
- + Membrane A, method EQUI.

TABLE I. GENERAL PROPERTIES OF MEMBRANES STUDIED

| | Membrane A (Progil C 892) | Membrane B furn. by E. Korngold (Neguev Institute Israel) |
|--|--|--|
| Type | Sulphonated polystyrene on a PTFE support | Sulphonated polyethyl- ene vapor phase |
| Capacity | 1.0 meq/g/s | 1.37 meq/g/s |
| Swelling rate (NaCl 0.1 M) | 15% | 65% |
| t_1 (NaCl 0.1 M) | 0.98 | 0.97 |
| Thickness (NaCl 0.1 M) | 0.060 mm | 0.260 mm |
| P_2 coefficient of permeability $\Delta C = 0.05$ | $3.7 \cdot 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$ | $3.8 \cdot 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$ |

1) Measurement and control of concentration profiles

Table II and Figure 2 show that there is no significant difference between the results obtained for the two membranes for the case of the method EQUI (maximum deviation 3%). This confirms the fact that in this case, osmosis and retrodiffusion do not intervene. Therefore, only the electrotransport properties control the polarization.

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On the other hand (Table III, Figure 2), the DICET method shows that there is a difference between the two membranes:

- for membrane A which swells only slightly and which has a very small permeability coefficient, the polarization curve is identical with the one found with the EQUI method (negligible influence of the retrodiffusion and osmosis);

- for membrane B, the polarization curve deviates from the preceding one and this is in agreement with a strong rate of swelling and a correspondingly higher permeability coefficient.

By utilizing (4), it is possible to calculate a permeability coefficient for the membrane B (unfortunately the error cannot be made smaller than 10%, because the calculation is made using the difference $I_E - I_D$).

For $\Delta C = 0.05$ we found

$$P_1 = 6,8 \cdot 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1} \pm 0,1 \cdot 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$$

It is interesting to compare P_1 with the value P_2 obtained for the same ΔC using a more classical method consisting of a measurement of the concentration variation in the most diluted compartment by allowing the system to evolve under the influence

TABLE II. RESULTS OBTAINED BY THE EQUI
METHOD FOR MEMBRANES A AND B.
REFERENCE CONCENTRATION C = 0.1 M NaCl. [*]

| ΔC moles/l | Membrane A I_E mA/cm ² | Membrane B I_E mA/cm ² | Devia- tion % |
|-----------------------|---|---|---------------------|
| 0,01 | 0,56 | 0,57 | - 2 |
| 0,02 | 1,24 | 1,21 | + 3 |
| 0,03 | 2,07 | 2,04 | + 2 |
| 0,04 | 3,00 | 3,00 | 0 |
| 0,05 | 3,95 | 3,95 | 0 |
| 0,06 | 5,0 | 5,1 | - 2 |
| 0,07 | 6,15 | 6,2 | - 1 |

* Translator's note: Commas in numbers represent decimal points.

TABLE III. POLARIZATION RESULTS OBTAINED BY THE DICET
METHOD FOR MEMBRANES A AND B.
CONCENTRATION C = 0.1 M NaCl [*]

| I mA/cm ² | ΔC membrane A | ΔC membrane B |
|-------------------------|--------------------------|--------------------------|
| 0,637 | 0,0107 | 0,0095 |
| 1,59 | 0,0246 | 0,0220 |
| 3,18 | 0,0420 | 0,0385 |
| 4,78 | 0,0580 | 0,0535 |
| 6,37 | 0,0720 | 0,0666 |
| 7,95 | 0,0833 | 0,0800 |

* Translator's note: Commas in numbers represent decimal points.

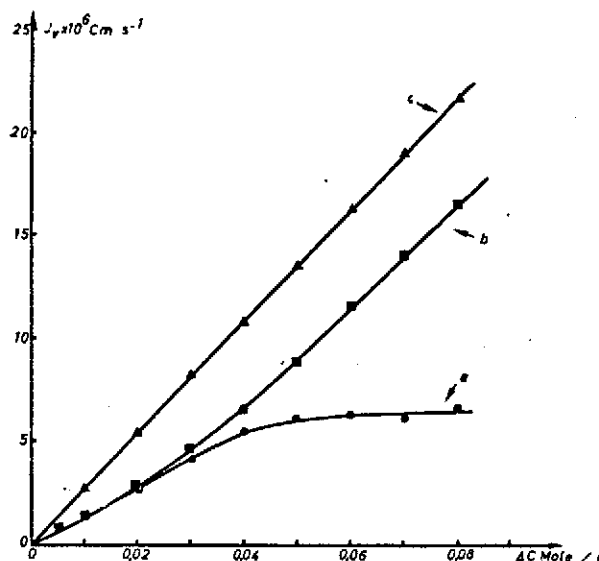


Figure 3. Variation of the water flux as a function of the concentration difference in the diffusion layers.

- Osmotic flux (a).
- Electroosmotic flux EQUI (b) method.
- ▲ Electroosmotic flux DICET (c) method.

of its own difference in electrochemical potential (profile a).

In this case for $\Delta c = 0.05$ we have

$$P_2 = 3,8 \cdot 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1} \pm 0,1 \cdot 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$$

P_2 and P_1 have the same order of magnitude, but P_1 is found with an electrical field and is therefore larger. It would be an illusion to discuss the causes for the deviation between these two coefficients within the framework of our experiments with any accuracy. Nevertheless, two qualitative explanations can be given for accounting for the fact that $P_1 > P_2$.

- the electroosmotic flux which is primarily involved for P_1 increases the apparent retrodiffusion because there is a tendency

to dilute the concentrated interface (profile c);

- the concentration gradients in the membrane when there is current are larger [24] in the case P_1 , which could produce an apparent increase in P_1 . Even though these interpretations seem reasonable, the deviations observed between P_1 and P_2 justify an additional study of this problem which would be more detailed.

These preliminary results show that the membrane B is particularly sensitive to the influence of the polarization of concentration which develops at the interfaces. Therefore, we studied water transport most of all using this membrane.

2) Measurement of the water transport

Table IV and Figure 3 compare the water fluxes obtained for the various profiles as a function of ΔC , whether this concentration difference is obtained by introducing two different concentrations or whether it is caused by an electrical field. We will analyze both curves in succession.

/825

a) Case of profile (a)

As Curve (a) in Figure 3 shows, the water flux is not proportional to ΔC and has a negative abnormal osmosis. This phenomenon is frequently observed with ion exchange membranes [11, 14].

This behavior can be explained by the strong dependence between the salt flux and the water flux.

Equation (12) shows that the volume flux consists of a contribution proportional to the concentration difference imposed and a flux which depends on the permeability of the salt of the system for a given concentration pair. Since the coefficients

ω and ξ of equations (12) and (13) can be considered in the first approximation as depending only slightly on the concentrations, one is led to conclude that there is a strong reduction in P_2 for large concentration gradients. This is generally observed for membranes which are quite highly charged [11].

This drop in P_2 can be attributed to the potential difference created by the concentrations on each side of the membrane.

b) Case of profile (b)

The curve (b) of Figure 3 shows the variation of the water flux as a function of ΔC . In this case, J_V , in agreement with (13), is essentially proportional to $\Delta c^{5/4}$.

The plot of the water transport coefficient (Figure 4, b), as a function of the current density shows that $t_{0(app)}$ is constant except for experimental errors [as predicted in (14)] within the studied range, and is equal to 12.]

It therefore seems that we have obtained the desired equal concentration.

As a comparison, we carried out measurements of electroosmotic fluxes with identical concentrations on both sides of the membrane, but we strongly agitated the solutions, as is usually done. In this case, we also found that the water transport coefficient was independent of the current density but it was equal to 19. This deviation can be explained by the fact that the concentration polarization can never be ignored and that one always has a profile of type (c).

According to Equation (16)

$$t_{od} = t_{oe}^* + \frac{2\omega F \Delta C}{V_0 I}$$

If the agitation produces a purely laminar convection, the ratio $\Delta C/I$ is independent of I up to an average polarization (50%). t_{oe}^* and ω can be considered as constants and in addition $t_{oe}^* \approx t_{oe}$. The change from 12 to 19 of the water transport coefficients will therefore be due to the second term in Equation (16). From this we find the importance of the ratio $\Delta C/I$ and the relationship between ΔC and I . In agreement with hydrodynamic calculations, the greater the convection becomes, the smaller the ratio $\Delta C/I$ becomes; however, in an experiment one cannot allow this parameter to become completely negligible. For example, we observed that for a linear flow velocity of the solution along the membrane of 20 cm.S^{-1} , we only obtain a depolarization of 75% for $I = 8 \text{ mA/cm}^2$.

The measurement of the water flux in the case of the profile of the method EQUI therefore results as a means of eliminating the systematic errors introduced by diffusion films. This then leads to a water transport coefficient which is purely due to electroosmosis.

c) Case of profile (c)

In this complex case, the water transport coefficient depends strongly on the current density (Curve C, Figure 4).

The discussion of the results in the case of profile (b) showed that the water transport is strongly affected by the ratio $\Delta C/I$.

TABLE IV ^{*}

| ΔC | Method EQUI | | | | Method DICET | | | | Osmosis |
|------------|------------------------------|---------------------------------------|-------------------|----------|------------------------------|---------------------------------------|-------------------|----------|---------------------------------------|
| | I_E mA cm^{-2} | J_V $\text{cm}^{-1} \times 10^3$ | $K_E \times 10^3$ | t_{OE} | I_D mA cm^{-2} | J_V $\text{cm}^{-1} \times 10^3$ | $K_D \times 10^3$ | t_{OD} | J_V $\text{cm}^{-1} \times 10^3$ |
| 0,01 | 0,57 | 1,11 | 3,94 | 11 | 0,605 | 2,60 | 3,75 | 23,1 | 1,43 |
| 0,02 | 1,21 | 2,47 | 4,31 | 11 | 1,4 | 5,47 | 3,84 | 20,9 | 2,6 |
| 0,03 | 2,04 | 4,56 | 4,26 | 11,8 | 2,3 | 8,2 | 3,87 | 18,9 | 4,17 |
| 0,04 | 3,00 | 6,64 | 4,17 | 11,9 | 3,35 | 10,9 | 3,92 | 17,5 | 5,33 |
| 0,05 | 3,95 | 8,85 | 4,18 | 11,8 | 4,45 | 13,7 | 3,80 | 16,5 | 5,98 |
| 0,06 | 5,1 | 11,6 | 4,09 | 12,2 | 5,6 | 16,4 | 3,80 | 15,7 | 6,24 |
| 0,07 | 6,2 | 14,1 | 4,08 | 12,15 | 6,74 | 19,1 | 3,82 | 15,2 | 6,12 |
| 0,08 | 7,3 | 16,5 | 4,1 | 12,1 | 7,95 | 21,7 | 3,83 | 14,6 | 6,7 |

* Translator's note: Commas in numbers represent decimal points.

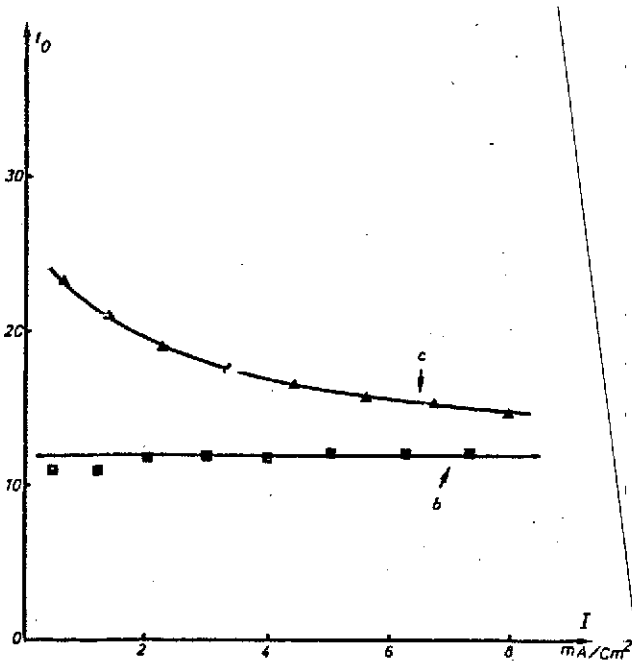


Figure 4. Variation of the water transport coefficient as a function of the density of the imposed current.

■ EQUI method.
▲ DICET method.

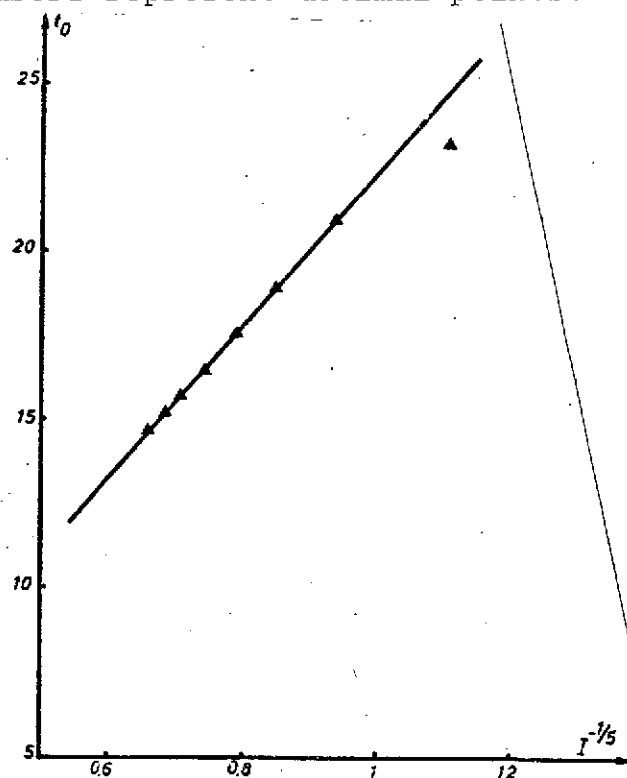


Figure 5. Variation of the water transport coefficient obtained by the DICET method as a function of $I^{-1/5}$ (the current density is expressed in mA.cm^{-2}).

We can find a relationship of the following type by an experiment and to a good degree of approximation (Table IV):

$$\Delta C \approx K_D I^{1/6} \quad (17)$$

[The difference between K_D and K_E which appears in Table IV is caused by the second term of Equation (3)].

By combining (16) and (17) we obtain

$$t_{OD} \approx t_{OE} + \frac{2\omega F K_D}{V_0} I^{1/6} \quad (19)$$

The plot of the transport coefficient as a function of $I^{-1/5}$ (Figure 5) leads to a straight line as the equation predicts.

Other authors observed a dependence between the water transport coefficient and the current density [4, 19]. Insufficient agitation at the membrane interfaces could explain this dependence.

This is particularly true for George and Courant [19] who indicate that in their experiments, one interface of a membrane is subjected to agitation.

Lakshiminarayanaiah and coll. [4] also want to eliminate the polarization and therefore utilize a pulse technique.

Unfortunately, the method which they proposed cannot withstand a chronopotentiometer analysis of the formation of the polarization layers.

The time required for establishing a polarization ΔC at the membrane interface is given by the expression

$$t = \frac{F^2 \pi D}{4(t_1 - t_0)^2} \left(\frac{\Delta C}{I} \right)^2$$

The term $\Delta C/I$ varies as a function of the convection which develops at the interfaces. It is easy to see that the diffusion layer reaches a quasi-stationary regime faster when the agitation becomes stronger.

If we carry out the calculation, for example, for the following natural convection conditions:

$$\begin{array}{l} \text{NaCl} = 10^{-2} \text{ M} \\ \Delta C = 5 \cdot 10^{-3} \text{ M} \\ I = 0,33 \text{ mA/cm}^2 \end{array} \quad \left| \right.$$

t found is 67 sec.

However, if $\Delta C/I$ is reduced by a factor of 10 because of a forced convection attack, the time becomes 0.67 sec.

Just like in the experiments of Lakshminarayanaiah, the current passage time is 30 sec and since the imposed convection seems to be in a zone somewhere between natural and forced convection (the authors unfortunately do not indicate the order of magnitude of their hydrodynamic layer), the polarization layers have time to form at the beginning of the experiment.

We believe that the variation in the water transport coefficient observed by these authors is caused by the polarization effect at the membrane interfaces. This polarization produces osmosis and retrodiffusion because of modifications to the interface concentrations.

CONCLUSION

We utilized a measurement method and control method for concentration profiles at interfaces so that we were able to measure pure electroosmotic flux through an ion exchange membrane.

As far as all the results of the literature are concerned, this method has the advantage of being able to isolate the fundamental influence of the polarization at the interfaces, and in particular, the effect of the ratio $\Delta C/I$ on the measured water transport coefficient.

The results obtained with the EQUI method lead to a water transport coefficient which is independent of the current density. This is in complete agreement with the theory for $(C_{(II)} - C_{(I)})$ equal to zero.

These measurements were carried out in natural convection by imposing equal interface concentrations. Therefore, it is not the convection regime which is important for obtaining pure electroosmosis, but the fact that the interface concentrations are equal.

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We also showed that the fact that one could find a water transport coefficient independent of I , and this for forced convection by ignoring the films, was still not a criterion for measuring pure electroosmosis.

In effect, in this case, according to the laws of hydrodynamics, $\Delta C/I$ is independent of I but $C_{(II)} - C_{(I)}$ is not zero. In agreement with Equation (17), the water transport coefficient is constant in this case but larger than the value which is obtained by the EQUI method because of the residual polarization. Consequently, one finds that the experimental conditions of the EQUI method are the only ones which agree with the theoretical requirement for measuring a purely electroosmotic flux.

This method still has one drawback for achieving a greater accuracy in the control of interface concentrations because neither forced convection nor natural vertical convection can bring about polarization layers which correspond to our model at

all points of the membrane surface. Nevertheless, the good results obtained seem to show that the concentration profiles are not dispersed too much. Improvements in the interface concentration control method are being developed.

In the case of the DICET method, i.e., when one follows the variation of the apparent water transport for a known polarization, the transport coefficient was found to be a function of $I^{-1/5}$. The ratio $\Delta C/I$ then can be used to determine this variation law by using the results of natural convection as an intermediary.

In all cases, the polarization data and the controls on the interface concentrations can be used to explain the nature of the curves obtained.

Consequently, we believe that certain uninterpreted results which have appeared in the literature can be explained by the fact that the authors did not introduce the influence of $\Delta C/I$ and therefore of the polarization, even though it was small (see IV, 2, c).

In particular, the dependence of the water transport coefficient on the current density indicated in the literature could be attributable to insufficient agitation for which $\Delta C/I$ is constant (intermediate zone between natural and forced convection).

A kinetic analysis based on the equations of Nernst-Planck was developed [29] and leads to conclusions which are in agreement with this approach. Nevertheless, this interpretation seems to be limited to membranes with a high charge density and with a moderate water permeability.

In the case of highly permeable membranes, recent results of Lorimer [30] could suggest other interpretations of the dependence

of the water transport coefficient on the current density.

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